# Electronic Properties of Oxidized Carbon Nanotubes

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The effect of oxygenation on the electronic properties of semiconducting carbon nanotubes is studied from first principles. The $O_2$ is found to bind to a single-walled nanotube with an adsorption energy of about 0.25 eV and to dope semiconducting nanotubes with hole carriers. Weak hybridization between carbon and oxygen is predicted for the valence-band edge states. The calculated density of states shows that weak coupling leads to conducting states near the band gap. The oxygen-induced gap closing for large-diameter semiconducting tubes is discussed as well. The influence of oxygen on the magnetic property is also addressed through a spin-polarized calculation and compared to experiment.

The electronic structure of a single-walled carbon nanotube (SWNT) is determined by the tube chirality and diameter [1]. It was believed that the electronic properties of SWNT are relatively insensitive to their chemical environment, especially to gas exposure because of the strong on-tube carbon-carbon $sp^2$ bonding and presumably weak interactions between the gas molecules and the carbon tubes. However, it has been demonstrated experimentally that the electronic properties of semiconducting SWNTs are extremely sensitive to their exposure to gas molecules [2–4]. Recently, there has been a series of experiments that measure the dependence of the electronic and transport properties of carbon nanotubes on oxygen exposure. It is found that not only the resistance of the nanotube mats shows a stepwise behavior because of oxygenation and deoxygenation, but also some small-gap semiconducting nanotubes exhibit metallic behavior when they are exposed to oxygen [2]. The thermoelectric power (TEP) of nanotube mats is also found to be very sensitive to oxygen exposure, and the TEP of oxygenated SWNT mats is unusually large compared to that of ordinary metals or graphite. Furthermore, even sign changes are observed because of oxygenation and deoxygenation [2,3]. Similar sensitivity to oxygen is also found in an NMR measurement where the spin lattice relaxation rate for a nanotube changes rapidly as oxygen is introduced [5]. Another important point that should be raised is the possibility that unintentional oxygen contamination during preparation of nanotubes may have lead to incorrect analysis of data in previous experiments. Therefore, understanding of the effects of oxygen on the electronic and transport properties of carbon nanotube is essential and timely not only for potential applications of nanotubes as molecular sensor, but also for resolving their true intrinsic properties.

In this Letter, we use the *ab initio* pseudopotential total energy method [6,7] to study the effect of oxygen on the electronic and magnetic properties of SWNTs. We focus on semiconducting carbon nanotubes since we expect that

oxygen exposure will have a much smaller effect on the properties of metallic armchair tubes. Some key questions are whether or not or how strongly $O_2$ binds to nanotubes, how the electronic structure is modified (especially how semiconducting nanotubes can become metallic), and how oxygen affects the magnetic properties of nanotube.

The *ab initio* total energy calculations were based on pseudopotential density functional theory [6,7]. We adopted the local density approximation (LDA) for the exchange-correlation potential. For the study of the spin-polarization effect of the oxygen molecule, we also used a local spin density approximation (LSDA). The cutoff energy for the expansion of the planewave basis is 50 Ry. We chose an (8,0) carbon nanotube and put one oxygen molecule in each unit cell to simulate the oxygen adsorption on semiconducting tubes. The center-to-center distance between nearest tubes in the supercell is 13.23 Å, which results in a distance of about 7 Å between the nearest carbon atoms on adjacent tubes.

On a graphite surface, $O_2$ adsorption results in basically two possible structural phases, $\delta$ (low density) and $\zeta$ (high density) phases at low temperatures [8]. The oxygen molecule in the $\delta$ phase lies parallel to the carbon-carbon bonding, while the molecular axis generally forms an oblique angle with the graphite surface in the $\zeta$ phase. Here we consider the $\delta$ phase as a plausible configuration for oxygen adsorption on a nanotube at moderate coverages. Among the many possible adsorption sites, a bridge site of carbon-carbon bonding parallel to the tube axis is chosen for the present calculation [9].

To examine the binding properties, we first studied the adsorption behavior of oxygen on nanotubes. In order to find the optimal adsorption distance, the total energy of the tube $+ O_2$ is calculated as a function of the distance between the oxygen molecule and the tube. For this purpose, we need to obtain a fully relaxed atomic configuration of the (8,0) carbon nanotube and the $O_2$ molecule separately. The bond length and stretching frequency of isolated $O_2$

molecule are found to be 1.197 Å and 1565 cm$^{-1}$, respectively, in good agreement with the experimental values of 1.207 Å and 1534 cm$^{-1}$ [10]. We then calculate the total energy of the tube + $O_2$ with the $O_2$ molecule on top of the bridge site with varying distances between the $O_2$ and the tube. At this stage, any atomic relaxation is not considered since the interaction between the nanotube and oxygen is presumably weak up to moderate distances. In fact, we find that the residual forces on all atoms for distances over ~2.4 Å are small enough ($\lesssim$0.2 eV/Å) so that any relaxation would not alter the overall shape of the total energy curve near the equilibrium position. At smaller distance, however, forces are not negligible and the total energy should be smaller for full atomic relaxation than that presented here (however, the optimal distance and binding energy will change very little) [11].

Figure 1 shows the result of our calculations of the binding energy ($E_b$) as a function of the distance ($d$),

$$E_b(d) = E_{\text{tot}}(\text{tube} + O_2) - E_{\text{tot}}(\text{tube}) - E_{\text{tot}}(O_2).$$

(1)

We calculated the total energy of oxygen in the same supercell geometry as used in the tube + $O_2$ system to minimize any artificial supercell effects. The optimal distance is found to be about at 2.7 Å, and the oxygen molecule binds to the (8,0) nanotube with an adsorption energy of about 0.25 eV. Our calculated binding energy shows that oxygen adsorption on nanotubes is in between chemisorption and physisorption. The large curvature of the (8,0) tube studied here may give strong chemical activity at the bridge sites. It is also well known that the LDA tends to overestimate the binding energy. However, we expect that to an order of magnitude the binding energy should be the same as our calculated value.

We have investigated how oxygen adsorption modifies the electronic structures of semiconducting carbon nano-tubes. Figure 2 shows the band structure of the tube + $O_2$ for $d = 2.7$ Å. The Fermi level lies at the zero of energy slightly below the top valence band states of the carbon nanotube. An isolated (8,0) carbon nanotube has a band gap of about 1 eV in the $\pi$-electron only model but the actual LDA band gap is reduced to about 0.6 eV due to the $\sigma - \pi$ hybridization. The flat bands (labeled by O1 and O2 in Fig. 2) at the Fermi level are derived from oxygen $pp\pi^*$ states and they are almost half filled. We observe a comparatively large splitting in the oxygen-derived states and the carbon states lying about 0.5 eV below the Fermi level at the $\Gamma$ point (labeled by C1 and C2 in Fig. 2). This large splitting of these carbon states is attributed to the adsorbate-tube interaction and the symmetry of these particular states.

Since the HOMO states of the oxygen molecule have $pp\pi^*$ antibonding character, the coupling will be sensitive to the bonding character of the carbon states at the adsorption site. A single (8,0) carbon nanotube has $D_{8h}$ symmetry and each carbon state has rotational and reflection symmetry depending on its bonding character [12]. The carbon states lying 0.5 eV below the Fermi level (C1 and C2 states in Fig. 2) have fourfold rotational symmetry along the circumferential direction and a $\pi^*$-like character along the bridge site. Coupling with oxygen can then be large and actually gives rise to about a 0.2 eV splitting in energy. On the other hand, the top valence band states (C0 states in Fig. 2) have $\pi$-like character at the bridge site. The interaction of these states with oxygen will be very small and so is the splitting (about 0.03 eV) which is hardly noticeable in the band structure. The symmetry-selective interaction of oxygen with the different carbon states implies that oxygen adsorption (diatomic molecular adsorption in general) may have a different behavior
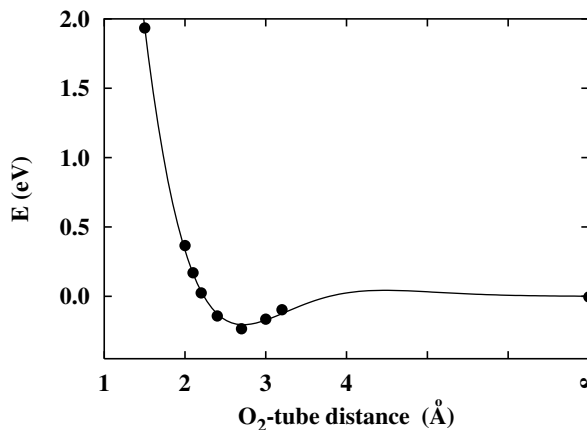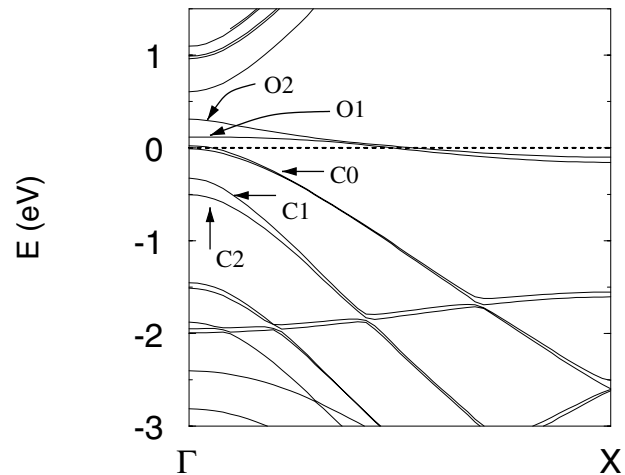


FIG. 1.   Binding energy curve of an oxygen molecule to a (8,0) carbon nanotube as a function of distance from oxygen to the tube. The solid curve is given as a guide.



FIG. 2.   Band structure of the (8,0) carbon nanotube + $O_2$. Only the states near the band gap are plotted. The Fermi level lies at the zero of energy. The flat bands (O1 and O2) lying at the Fermi level are derived primarily from oxygen molecular states. Note the comparatively large splitting of oxygen states (O1 and O2), and of the carbon states (C1 and C2) at $E = \sim -0.5$ eV.

depending on the chirality and diameter of the tube at low temperatures.

Figure 3 shows squared wave functions of the states (C2 and O2 states in Fig. 2) near the Fermi level that have comparatively strong coupling between carbon and oxygen as mentioned above. The plot is drawn in the plane perpendicular to the tube axis passing through one of the oxygen atoms. Weak bonding-like and antibonding-like characters are apparent between carbon and oxygen. As discussed below, the weak coupling has a profound effect on the conductance of the nanotube.

The calculated density of states (DOS) of the oxygen-doped carbon nanotubes is shown in Fig. 4 [13]. Sharp peaks at the band edge are typical of 1D density of states. Two small peaks near the Fermi level, which is taken as the zero of energy, come from the valence band top states derived from carbon. Note that the Fermi level lies about 0.01 eV below the upper peak of the carbon-derived states, which indicates that oxygen can dope semiconducting tubes giving hole carriers and finite conductance. This finding is consistent with a recent experiment on the resistance of SWNT mats where a stepwise change in resistance is observed upon oxygenation and deoxygenation [2]. From a population analysis, we estimated that about 0.1 electron is transferred from the carbon nanotube to each oxygen molecule. The 1D features of the DOS and the enhancement of the conductance of the oxygen-doped semiconducting tube are found to be a possible source for the observed large TEP and its sensitivity to oxygen [3].

The dashed line in Fig. 4 denotes the partial DOS projected onto the carbon nanotube. We note that a small tail in the carbon projected DOS persists up to 0.3 eV above the Fermi level. The coupling with oxygen gives a nonzero value for the carbon partial DOS even above the Fermi level, and a conduction can occur through the tail states. Scanning tunneling spectroscopy which can be used to measure the local density of states yields a small

but clear increase in the density of states as the semiconducting nanotube is exposed to oxygen [2]. Our results suggest that a small-gap semiconducting nanotube can exhibit metallic behavior at moderate oxygen doping and thus is consistent with experiment.

The ground state configuration of the oxygen molecule is $^3\Sigma_g^-$ where two electrons of the same spin occupy each of the $pp\pi^*$ states [14]. The excitation energy to the singlet states, $^1\Delta_g^+$ and $^1\Sigma_g^+$, is about 0.98 and 1.63 eV, respectively, which is much larger than the binding energy obtained here. It is therefore expected that $O_2$ remains as a spin-triplet state on the tube surface. We carried out LSDA-based total energy calculations and found that the oxygen molecule is in the spin-triplet state at the equilibrium distance obtained from the LDA calculation ($\sim 2.7$ Å). The spin-triplet state is lower in energy by about 1 eV than the singlet state in our calculations. The oxygen molecular states (O1 and O2 states in Fig. 2) split, and the spin-up states are fully occupied and the spin-down states are nearly empty. A similar charge transfer (0.1 electron to an $O_2$ molecule) occurs, giving a finite density of states at the Fermi level. Therefore, we expect that oxygenation can have a significant influence on the magnetic responses of nanotubes. In a recent NMR measurement, it is found that the spin-lattice relaxation rate of carbon nanotubes becomes much faster when the tubes are exposed to oxygen [5]. In contrast, other diatomic molecules such as $H_2$ and $N_2$ have very little effect on the spin lattice relaxation. We comment that the spin configuration of the oxygen molecule may depend on its binding character to the carbon nanotube. Strong binding of chemisorbed oxygen would prefer a spin-singlet state while physisorbed oxygen favors the spin-triplet state. Oxygen molecules bound strongly at chemically active
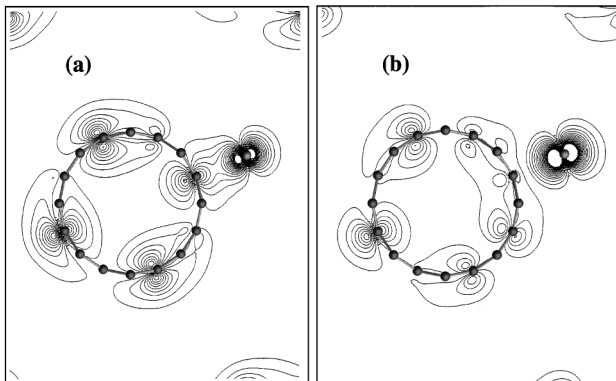


FIG. 3. Squared wave function of weakly hybridized states between carbon and oxygen orbitals at the Γ point in the band structure; (a) bonding-like state (labeled C2 in Fig. 2) and (b) anti-bonding-like state (labeled O2 in Fig. 2). The plotting plane is normal to the tube axis and passes through one of the oxygen atoms.
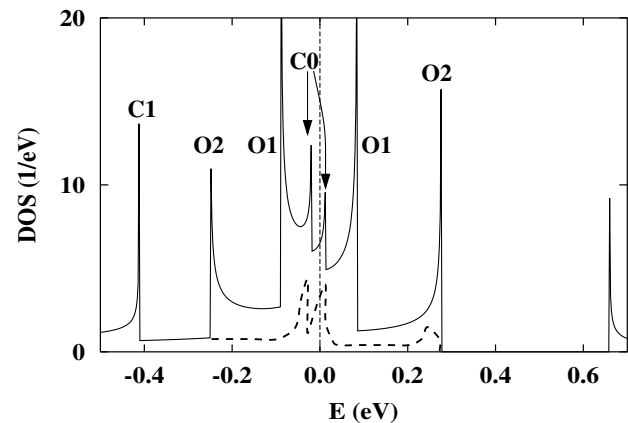


FIG. 4. Density of states of oxygen doped (8,0) carbon nanotube. The Fermi level is at the zero of energy. Two small sharp peaks (C0's) near the Fermi level come from the top valence band states (derived from carbon states). Other peaks labeled come from the corresponding states in the band structure (Fig. 2). The dashed curve is the partial DOS projected on to carbon nanotube. The small but finite tail of the carbon partial DOS persists up to 0.3 eV above the Fermi level.

sites are expected to have little effect on the magnetic responses.

In summary, we studied the effect of oxygenation on electronic and transport properties of carbon nanotubes from first principles. The $O_2$ adsorbs on tube wall with a binding energy of about 0.25 eV and a binding distance of $\sim 2.7$ Å. A charge transfer of about 0.1 electron from the carbon nanotube to every oxygen molecule is predicted. The LSDA calculation shows that the $O_2$ molecules adsorbed on nanotubes remain in spin-triplet states and can influence the magnetic properties of carbon nanotubes significantly.

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[11] At $d = 1.5$ Å, we performed atomic relaxation and found that an oxygen molecule tends to dissociate. However, we did not do a full relaxation calculation since the artificial supercell interaction may be dominant at this stage.

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